is in plane with the rest of the molecule and its π molecular orbitals extend over the whole molecule. However, in benzylideneaniline itself, the Ph_N ring is out of plane and therefore the shift caused by substituting the methyl group in *N*-benzylimine by a phenyl group is small compared to the shift caused by a similar substitution in *N*-benzylimine conjugate acid.

Comparing the spectrum of styrene and *trans*-stilbene, it is clear that phenyl group substitution in styrene shifts the absorption band by 6424 cm^{-1} to the red, which is comparable to the red shift (5924 cm^{-1}) observed when the methyl group in the *N*-benzylimine conjugate acid is replaced by a phenyl group which presumably assumes a planar configuration.

A large (about 7000 cm^{-1}) red shift of the CT band of benzylideneaniline is observed due to protonation. The value of this shift is obtained by comparing the CT band maxima of benzylideneaniline in alcohol and in concentrated sulfuric acid and by taking into consideration medium effects. The latter are estimated by comparing the CT band maxima of *N*-benzylimine in alcohol + HCl and in concentrated sulfuric acid. This shift is due in part to the positive charge on the nitrogen atom and also to having the phenyl group of the aniline part assume a coplanar configuration in the conjugate acid. Similar red shifts have been observed[13] as a result of protonation of carbon tetrachloride solutions containing retinal (vitamin A aldehyde) and a secondary amine, *e.g.*, diphenylamine, indole, carbazole, and piperidine. These results were interpreted in terms of the formation of enamine salts of retinal with secondary amines.

Energy calculation[14] of CT and LE states of Schiff's bases using a localized orbital model provides further support for our assignments of the electronic transitions of benzanils. Also, the study of the absorption spectra of *N*-benzylimines[15] and their interaction with iodine gives more evidence that in benzanils the lone-pair electron on the nitrogen atom is conjugated to the phenyl group.

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(13) J. Toth and B. Rosenberg, *Vision Res.*, **8**, 1471 (1968).
(14) M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, manuscript in preparation.
(15) M. El-Aasser, F. Abdel-Halim, and M. A. El-Bayoumi, *J. Amer. Chem. Soc.*, **93**, 590 (1971).

Electronic Spectra and Structures of Schiff's Bases. II. *N*-Benzylimines[1]

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Abstract: Electronic absorption spectra of substituted *N*-benzylimines have been measured at room temperature in different media. The spectra support our interpretation of the spectra of benzanils as being essentially a superposition of the spectra of the corresponding benzal and aniline parts of the molecule. It is shown that the azomethine group acts as an electron acceptor when linked to a phenyl group at its carbon end and as an electron donor when linked to a phenyl group at its nitrogen end. Iodine interaction with *N*-benzylimine in carbon tetrachloride indicates that the lone pair of electrons on the nitrogen are more available to interact with iodine than in benzylideneaniline.

Electronic absorption spectra of benzanils have been interpreted in terms of two weakly interacting moieties of the molecule, namely the benzal and aniline parts. The various absorption bands were assigned[4] to transitions involving locally excited states (LE) or to intramolecular charge-transfer states (CT) of the benzal and aniline parts. We have measured the absorption spectra of substituted benzylimines in different media. In benzylimines, the phenyl group is substituted with an aliphatic group. This will help in distinguishing electronic transitions involving the aniline part, which should be absent in the spectra of *N*-benzylimines, from those transitions involving the benzal part.

Experimental Section

Ultraviolet absorption spectra were measured at room temperature with a Zeiss PMQ II manual spectrophotometer. All solvents were extensively purified by standard procedures. *N*-Methylbenzylimine (bp 183–185°) and *p*-methoxy-*N*-methylbenzylimine [bp 112° (2 mm)] were prepared using the following procedure.[5] The corresponding aldehyde was treated slowly with excess aqueous solution of methylamine and allowed to stand overnight. The oily condensation product was then extracted with ether, sodium chloride was added, and the ether extract was dried over anhydrous calcium sulfate. Ether was evaporated, the residual oil was fractionally distilled under vacuum, and the boiling point of the oil was determined.

p-Hydroxy-*N*-methylbenzylimine (mp 178°) was prepared[6] by dissolving *p*-hydroxybenzaldehyde in hot alcohol; excess 33% aqueous methylamine at about 40° was added rapidly and the resulting solution was cooled in an ice bath for 2 hr. The crystalline product was filtered and washed with cold 40% alcohol and water, and its melting point was determined.

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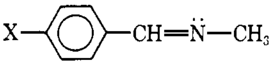
(1) Part of this work was carried out at the Biophysics Department, Michigan State University, under Contract No. AT(11-1)-2039, Division of Biology and Medicine, U. S. Atomic Energy Commission.
(2) The major portion of this work is from the M.S. thesis of M. El-Aasser, Alexandria University, Sept 1966.
(3) Biophysics Department, Michigan State University, East Lansing, Mich. 48823.
(4) M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Amer. Chem. Soc.*, **93**, 586 (1971).
(5) N. H. Cromwell, R. S. Babson, and C. E. Harris, *J. Chem. Soc.*, **65**, 313 (1943).
(6) N. H. Cromwell and H. Hoeksma, *J. Amer. Chem. Soc.*, **67**, 1658 (1945).

Table I. Absorption Maxima[a] (Å) and ϵ Values of Substituted *N*-Benzylimines in Alcohol Solutions



$X{-}C_6H_4{-}CH{=}\ddot{N}{-}CH_3$

Substituent X	Band I			Band II			Band III		
	λ_{max}	$\epsilon \times 10^{-3}$	$\Delta\bar{\nu}$, cm^{-1}	λ_{max}	$\epsilon \times 10^{-3}$	$\Delta\bar{\nu}$, cm^{-1}	λ_{max}	$\epsilon \times 10^{-3}$	$\Delta\bar{\nu}$, cm^{-1}
H	2900	0.8	0	2450	12.4	0	2050	21.9	0
OCH_3	(2960)	5.7	−699	2670	17.0	−3360	2150	14.4	−2270
OH	(2930)	6.9	−926	2680	17.9	−3500	2160	15.2	−2480

[a] Wavelengths enclosed in parentheses indicate a shoulder rather than a band maximum.

Table II. Comparison of the Absorption Spectra of Benzaldehyde, Styrene, *N*-Benzylimine, Propionaldehyde Anil, and *N*,*N*-Dimethylaniline in Hydrocarbon Solvent

Molecule	Formula	First absorption band λ, Å	First absorption band ϵ	Second absorption band λ, Å	Second absorption band ϵ
Benzaldehyde	$Ph{-}CH{=}O$	2870	1000	2410	14,000
Styrene[a]	$Ph{-}CH{=}CH_2$	2780	900	2480	15,000
N-Benzylimine	$Ph{-}CH{=}\ddot{N}{-}CH_3$	2770	900	2440	13,000
Propionaldehyde anil[a]	$Ph{-}\ddot{N}{=}CH{-}C_2H_5$	3020	2700	2490	13,000
N,*N*-Dimethylaniline	$Ph{-}\ddot{N}(CH_3)_2$	2980	2380	2510	15,800

[a] J. N. Murell, "The Theory of Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963.

Results and Discussion

Room-temperature absorption spectra of substituted *N*-benzylimines in alcohol are shown in Figure 1; the absorption data are summarized in Table I. The 3110-Å band observed for benzylideneaniline is absent in the spectra of *N*-benzylimine. This further supports its assignment as a locally excited transition which involves the aniline part of benzylideneaniline. The 2620-Å band in benzylideneaniline corresponds probably to the 2450-Å band in *N*-benzylimine. This band corresponds to a transition to a CT state in which the phenyl group acts as an electron donor and the azomethine group as an electron acceptor. Its displacement to higher energies (+2887 cm^{-1}) when the phenyl group is replaced by a methyl group at the nitrogen end of the azomethine group may reflect the effect of the phenyl group in increasing the electronegativity of the nitrogen atom and making the azomethine group a better electron acceptor. The first and third bands correspond to $^1B_{2u}$ and $^1B_{1u}$ locally excited benzene states, respectively.

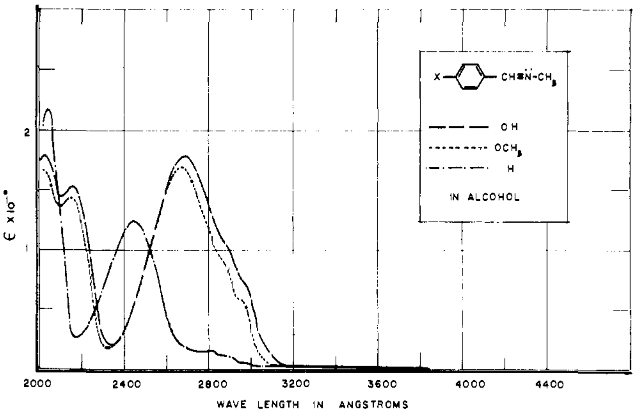


Figure 1. Room-temperature ultraviolet absorption spectra in alcohol of *N*-benzylimine with different substituents.

Large shifts are observed for the second and third bands of *N*-benzylimines as a result of substitution. The second band is particularly sensitive to substitution, an indication of its predominant charge-transfer character. It should be pointed out here than an n → π* transition of the unconjugated azomethine group occurs[7] at 2360 Å with an extinction coefficient around 100. This transition is expected to be hidden under the more intense transitions occurring at the same energies.

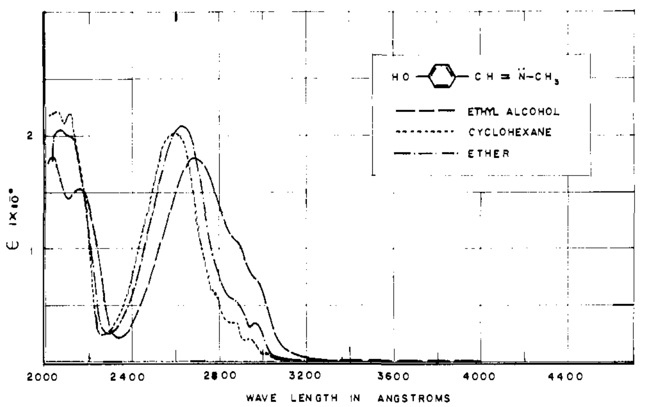


Figure 2. Room-temperature ultraviolet absorption spectra of *p*-hydroxy-*N*-benzylimine in different solvents.

The spectrum of *N*-benzylimine is similar to that of benzaldehyde and styrene, as shown in Table II. The clear similarity of styrene and imine spectra suggests that the band observed at 2440 Å in the spectrum of *N*-benzylimine corresponds to an electron promotion from the highest filled π MO of the ring to the substituent. The close similarity of the propionaldehyde anil and the *N*,*N*-dimethylaniline spectra suggests that the CT band occurs as a result of an electron promotion from the N atom lone pair to the ring. In short, the azomethine group acts as an electron acceptor when linked to a phenyl group at its carbon end and as an electron donor when linked to a phenyl group at its nitrogen end.

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(7) R. Bonnett, N. J. David, J. Hamlin, and P. Smith, *Chem. Ind. (London)*, 46, 1836 (1963).

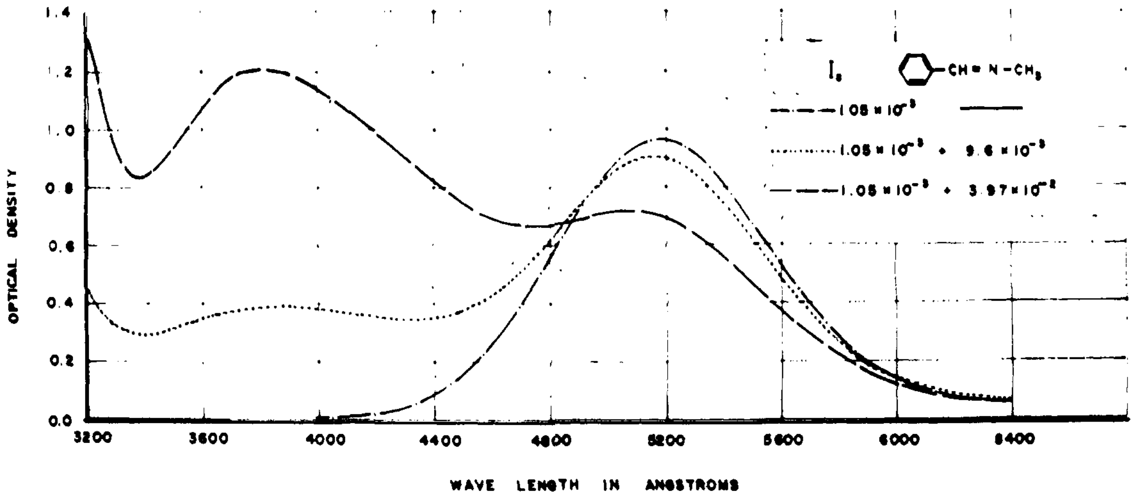

Figure 3. Room-temperature ultraviolet absorption spectra of a mixture of iodine and *N*-benzylimine in various concentrations in carbon tetrachloride; reference used is carbon tetrachloride containing the same concentration of *N*-benzylimine as in solution.

It is known[8] that the CT band observed at 2510 Å in *N*,*N*-dimethylaniline decreases in intensity as a result of steric crowding. Therefore the intensity of the 2490-Å band in propionaldehyde anil is expected to decrease as the overlap between the N lone-pair electrons and the phenyl ring decreases. In benzylideneaniline, where the Ph_N ring is probably neither planar nor perpendicular to the plane of the benzal part, such a band is expected to be less intense and partially hidden by more intense bands. The 2490-Å band of propionaldehyde anil corresponds possibly to the shoulder that appears at 2380 Å in benzylideneaniline.

Solvent effects on *p*-hydroxy-*N*-benzylimine are shown in Figure 2. The band at 2600 Å undergoes a relatively large red shift (-1147 cm^{-1}), indicating its CT character.

Iodine Interaction. Iodine forms a charge-transfer complex with *N*,*N*-dimethylaniline[9] in which the latter acts mainly as an n-electron donor. The visible iodine band shifts to the blue in the complex, and this shift is greater the larger the basicity of the base. Moreover, a CT band appears in the near-ultraviolet, the energy of which is determined by the ionization potential of the donor, the electron affinity of the acceptor, and the coulombic attraction between the electron and the hole left behind.

While in *N*-benzylimine the lone-pair electron on the nitrogen atom does not interact with the π system, in benzylideneaniline the lone pair conjugates with the Ph_N ring. Thus benzylideneaniline is expected to be less basic than *N*-benzylimine, and the latter should behave as a better n-electron donor.

We have studied the iodine complex formation with *N*-benzylimine in order to compare the results with previously reported data[10] on benzylideneaniline. The spectra of mixtures of iodine and *N*-benzylimine in various concentrations in carbon tetrachloride are shown in Figure 3. The reference used is carbon tetrachloride containing the same concentration of *N*-benzylimine. From the change in the optical density of the visible iodine absorption at 5200 Å, the equilibrium constant was deduced to be about 10, a value much larger than the reported value of 2.0 for benzylidineaniline. This gives further evidence that the lone-pair electron on the nitrogen atom in benzanils is conjugated with the Ph_N ring.

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(8) W. R. Remington, *J. Amer. Chem. Soc.*, 67, 1838 (1945).
(9) H. Tsubomura, *ibid.*, 82, 40 (1960).
(10) N. Ebara, *Bull. Chem. Soc. Jap.*, 33, 540 (1960).